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54 Method for treating ozone layer depleting substances.

57 A method for treating ozone layer depleting substances, in which a gaseous composition comprising helium or argon or a mixture thereof, or a gaseous mixture of argon and acetone, is introduced into a plasma reactor having a dielectric-coated electrode comprising a solid dielectric disposed on the surface of at least one of opposing electrodes, an atmospheric pressure glow discharge is generated in the gaseous atmosphere, gaseous ozone layer depleting substances are introduced into the glow discharge to decompose the substances, and resulting decomposition products are absorbed in water.

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## FIELD OF THE INVENTION

This invention relates to a method for treating substances which are destructive to the earth's ozone layer, more specifically, to a method for treating chlorofluorocarbon (CFC) compounds.

## DESCRIPTION OF PRIOR ART

Presently, ozone layer depleting substances are considered to include mainly CFC compounds, and thus they are called to be fully disused by 1955. However, at present, CFC compounds are used in a variety of applications such as car coolers and refrigerators, and the compounds must therefore be recovered and made harmless. In particular, specific CFCs which have chlorine in the molecule such as those of monofluoromethane (R-11), difluoromethane (R-12), trifluorotrichloroethane (R-113), tetrafluorodichloroethane (R-114), pentafluoromonochloroethane (R-115), and tetrafluoroethane (CFC-134) are difficult to be decomposed.

Recently, a method has been proposed as a means for decomposing CFC compounds, in which the compounds are decomposed by a high-temperature plasma at 10,000°C. However, this method requires generation of a very high temperature of 10,000°C, and involves problems which have yet to be solved before practical application in view of the treatment apparatus and treatment cost.

On the other hand, the inventors have proposed previously a method in which glow discharge is generated in a mixture of argon and helium or a mixture of a argon and a ketone under atmospheric pressure to excite a plasma, which makes the surface of substances hydrophilic or hydrophobic (Japanese Patent Publication Laid-open 3-23475, USP 5124173).

## OBJECT OF THE INVENTION

The inventors have intensively studied on means for decomposing gaseous ozone layer depleting substances, especially CFC compounds to be harmless, and found that the CFC compounds can be efficiently decomposed by an atmospheric pressure plasma which the inventors previously invented, accomplishing the present invention. Therefore, a primary object of the present invention is to provide a method for decomposing ozone layer depleting substances, especially CFC compounds containing chlorine which are perfectly gaseous at normal temperature and pressure, or under an increased or reduced pressure close to atmospheric pressure into hydrogen chloride and hydrogen fluoride, which are absorbed in water, that is, to provide a method for decomposing ozone layer depleting substances containing chlorine, especially CFC compounds, which is also advantageous in economy.

## SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a method in which a gaseous composition comprising helium or argon or a mixture thereof, or a mixture of argon and acetone, is introduced into a plasma reactor having a dielectric-coated electrode comprising a solid dielectric disposed on the surface of at least one of opposing electrodes, an atmospheric pressure glow discharge is generated in the gaseous atmosphere, gaseous ozone layer depleting substances are introduced into the glow discharge to decompose the substances, and resulting decomposition products are absorbed in water.

In the present invention, as in the atmospheric pressure plasma treatment method invented by the inventors, an atmospheric pressure glow discharge is generated in an inert gas such as helium, argon, argon and a ketone, or nitrogen, gaseous ozone layer depleting substances, especially, CFC compounds in the state of gas or vapor are introduced in the glow discharge to be decomposed, hydrogen chloride and hydrogen fluoride produced by decomposition are absorbed in water and disposed of as hydrochloric acid and hydrofluoric acid, and the inert gas such as helium, argon, argon and ketone, or nitrogen is reused for glow discharge generation. Thus, the present invention provides a method for decomposing gaseous ozone layer depleting substances, especially CFC compounds, which is very economical and practical, in which gaseous ozone layer depleting substances such as CFC compounds, especially those CFC compounds containing chlorine are decomposed, and the decomposition products are absorbed in water, or in an aqueous acid solution.

The present invention will now be described in detail.

Gaseous ozone layer depleting substances in the present invention are those compounds which are destructive to the ozone layer, especially CFC compounds containing chlorine. Specifically, these compounds include monofluoromethane (R-11), difluoromethane (R-12), trifluorotrichloroethane (R-113),

tetrafluorodichloroethane (R-114), pentafluoromonochloroethane (R-115), tetrafluoroethane (CFC-134), and the like. Furthermore, the present invention can also treat those compounds which are out of the regulation but are considered to be destructive to the ozone layer such as trifluoromethane (R-3), monofluoropentachloroethane (R-111), and monofluoropentachloropropane (R-211), and ozone layer depleting substances other than CFC compounds such as 1,1,1-trichloroethane and perchloroethylene.

In the treatment of these gaseous compounds, the compounds or their vapors are introduced into an atmospheric pressure plasma generation apparatus. Depending on the size of the apparatus, the rate of introduction is preferably 200 cc to 1,000 cc/min as vapors of the compounds for an apparatus shown in the embodiment.

Plasma generation conditions in the atmospheric plasma generation apparatus will be described.

As a power supply for generating a glow discharge, a frequency of 50 Hz to 100 KHz, or 13.56 MHz which is approved to be used other than broadcast frequencies, can be used. Of these frequencies, 200 Hz to 50 KHz is preferable to achieve a temperature lower than 100°C close to room temperature, and 3 KHz to 10 KHz is the best for 30 to 60°C and room temperature.

Furthermore, depending on the type of gas and the gap between the electrodes, the voltage is normally 1,000 to 8,000 V.

To generate an atmospheric pressure plasma, it is necessary to generate glow discharge in the apparatus in the presence of an inert gas such as helium, argon, or a mixture of argon and a ketone. For all argon atmosphere, it is necessary to add a small amount of ketone vapor but, for decomposing 1,1,1-trichloroethane, stable glow discharge can be generated without the additional of ketone, and trichloroethane is decomposed to a water-soluble substance such as hydrochloric acid. In this case, even with trichloroethane added to argon gas in an amount of several ppm to 15%, the glow discharge continues stably, and it is unnecessary to add a gas for facilitating glow discharge generation such as a ketone or helium which has heretofore been indispensable for generating glow discharge in argon.

Furthermore, for 1,1,1-trichloroethane, it is not clear why the glow discharge generation is facilitated, but for CFC R-113, which has similar boiling temperature, no discharge is generated when it is added to argon alone, and the substance is not decomposed. Therefore, for CFC R-113, it is necessary to use helium as in the embodiment, or a mixture of argon and helium or argon and a ketone.

Decomposition products resulted from the decomposition by the atmospheric pressure plasma are absorbed in water. That is, the decomposition products are mainly fluorine compounds or chlorine compounds which are readily absorbed in water to form hydrochloric acid or hydrofluoric acid. These acids are dissolved in water and neutralized, removed in the form of sodium salts, undecomposed gas is contained in an atmospheric pressure tank, and recirculated in the glow discharge for reuse.

A number of glow discharge tubes can be connected in series to completely remove residual fluorine compounds and chlorine compounds, providing a very economical method.

Then, an apparatus for carrying out the present invention will be described with reference to the drawings.

Fig.1 is a schematic view of an atmospheric pressure plasma generation apparatus used in the present invention, Fig.2 is a schematic vertical cross sectional view of the apparatus, and Fig.3 is a schematic view for explaining the treatment method according to the present invention. Fig.4 is a schematic side view of an example of electrode used in the present invention, and Fig.5 is a schematic perspective view of another example of atmospheric pressure plasma generation apparatus used in the present invention.

Referring to Fig.1, a metal thin plate 2 is wound around the outside of a glass-made cylindrical tube 1 to form one electrode. A metal rod 3 is positioned on the center line of the cylinder of the glass-made cylindrical tube 1 to form the other electrode, and the individual electrodes are provided with connection terminals 6 and 7, respectively. T-formed glass tubes 4 and 5 are engaged with both ends of the glass-made cylindrical tube 1, one of which is used as a gas inlet port and the other is used as a gas outlet. A port which is on the center line of the glass-made cylindrical tube 1 is used as a support of the metal rod, the port is closed, and the other port is connected to the plasma generation apparatus.

In the apparatus of the above construction, when a high voltage is applied to both the electrodes, the glass of the glass-made cylindrical tube 1 functions as a dielectric and, as shown in Fig.2, glow discharge is generated in the cylinder. Examples of the conditions for generating glow discharge as follows: As shown by the arrow of Fig.3, helium gas is introduced from one port of the T-formed tube 4 and discharged from one port of the T-formed tube 5, and a voltage of 3KHz, 2,500 V is applied between the metal thin plate 1 and the metal rod 3. As a result, glow discharge is generated in the cylinder to form a plasma. In this case, the current was 30 mA and the output was 80 W.

In the present invention, the reactor tube inside is under an increased pressure or reduced pressure close to atmospheric pressure. When a gas is introduced from a gas inlet port 4 in Fig.3, the cylinder inside

is under an increased pressure due to a resistance during passage of the gas through a water absorption vessel or, when the gas is introduced from the port 4 under suction by a pump from the gas outlet port 8, the cylinder inside is under a reduced pressure. Glow discharge is generated at a lower pressure but, in the present invention, rather than a vacuum, the reduced pressure means a pressure close to atmospheric pressure up to 500 torr where the atmospheric pressure is 760 torr.

As an example of electrode used in the above apparatus, it is preferable to use a belt-formed metal thin plate wound around the outside of the glass cylinder as shown in Fig.4 because glow discharge in the glass tube is well visible.

Since the above apparatus is an example, and the introduction of CFC into glow discharge is a means for decomposition, vertical electrodes as shown in Fig.5 or electrodes covered by a number of dielectrics in a large vessel as in a Cottrell precipitator can also be used, rather than a cylinder.

Furthermore, since glass is weak to hydrogen fluoride to be corroded and is short in service life, an acid-resistant resin such as polyester, ABS, methacrylic, polyimide, AS, or fluororesin may be used. These resins are good dielectrics.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 is a schematic view showing an atmospheric pressure plasma generation apparatus used in the present invention.

Fig.2 is a schematic vertical cross sectional view showing the atmospheric pressure plasma generation apparatus shown in Fig.1.

Fig.3 is a schematic view for explaining the treatment method according to the present invention.

Fig.4 is a schematic side view showing an example of electrode used in the present invention.

Fig.5 is a schematic perspective view showing another example of atmospheric pressure plasma generation apparatus used in the present invention.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

Embodiments of decomposing vapors of CFC solvents using the above apparatus will now be described.

##### Example 1

A low-boiling CFC solvent for device cleaning was placed in a gas washing bottle, helium was passed through the bottle to produce a mixture of vapor of the CFC solvent and helium, and the mixture was introduced into the cylinder from the T-formed tube 4. In this case, the chlorine-containing CFC compound of about 10% by volume was mixed with helium, which was immediately decomposed to hydrogen chloride and hydrogen fluoride which are quite harmless to the ozone layer. The effluent gas was introduced into water contained in a decomposition product absorption vessel 6 as shown in Fig.3 to convert the hydrogen chloride and hydrogen fluoride to hydrochloric acid and hydrofluoric acid, respectively. The pH value of the water changed from 7 to 1-2 immediately after passing the effluent gas through the water, showing an acidic nature.

When a glass rod with ammonia water was brought closer to the effluent gas, white smoke of ammonium chloride was generated, showing the presence of hydrogen chloride resulted from decomposition of the CFC.

Although the decomposition rate depends upon the gas flow rate and speed through the cylinder, the apparatus used in the above embodiment had a length of discharge portion of 500 mm and an inner diameter of glass cylinder of 16 mm, when the CFC/helium mixture containing 10% CFC was passed at a rate of 5 liters/min, the decomposition rate was about 34% and, for a rate of 2 liters/min, the decomposition rate was greater than 60%, showing the high effectiveness of the present treatment method.

Table 1 shows gas chromatographic charts of untreated and treated CFC-mixed helium and plasma-treated CFC-mixed helium.

The sample gas for gas chromatography was sampled at the outlet of the plasma treatment tube (e.g. 5 in Fig.3).

Table 1

## Untreated

PKNO	TIME	AREA	MK	IDONO	CONC
1	0.05	230			0.0242
2	0.442	948423	V		99.9758
TOTAL		948653			100

## Treated

PKNO	TIME	AREA	MK	IDONO	CONC
1	0.442	605290			97.3399
2	0.525	16026	V		2.5772
3	0.808	516	V		0.0829
TOTAL		621831			100

Furthermore, as shown in Fig.3, after hydrogen chloride and hydrogen fluoride as decomposition products are removed, helium can be dried from the tube 7 for reuse at a very low running cost.

## Example 2

Helium was mixed with 1,1,1-trichloroethane, and treated at a flow rate of 5 liters/min in the same CFC decomposition apparatus as above. As a result, the decomposition rate was about 26%. Similarly, when 1,1,1-trichloroethane was mixed with argon and treated at a flow rate of 3 liters/min, the decomposition rate was as high as nearly 75%. This is shown in Table 2.

Table 2

## Untreated

5	PKNO	TIME	AREA	MK	IDONO	CONC
	1	0.72	189			0.025
10	2	1.098	1957	V		0.2584
	3	1.933	10168	V		1.3427
	4	2.372	744955	V		98.374
15	TOTAL		757269			100

## Treated

20	PKNO	TIME	AREA	MK	IDONO	CONC
	1	0.125	2062			0.971
	2	0.467	3808	V		1.7938
25	3	0.672	540			0.2546
	4	1.075	416			0.1958
30	5	1.758	183			0.0864
	6	2.357	205134	V		96.6237
	7	4.525	158			0.0747
35	TOTAL		212302			100

Furthermore, when argon was not dried to contain water and treated similarly, the decomposition rate was even further improved to 80%. This is shown in Table 3.

Table 3

## Untreated

5	PKNO	TIME	AREA	MK	IDONO	CONC
	1	0.282	2575			0.3221
10	2	0.683	538	V		0.0673
	3	1.082	234			0.0293
	4	2.362	796045			98.5813
15	TOTAL		799392			100

## Treated

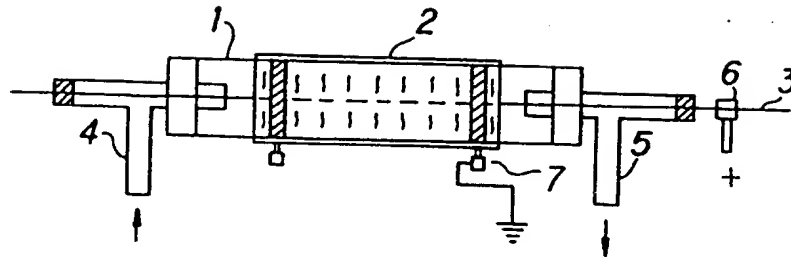
20	PKNO	TIME	AREA	MK	IDONO	CONC
	1	0.473	3454			1.4863
	2	0.557	347	V		0.1493
25	3	0.692	657	V		0.2827
	4	1.1	350			0.1508
30	5	1.758	1638			0.7051
	6	2.378	225644	V		97.1011
	7	4.582	290			0.1248
35	TOTAL		232380			100

As described above, the present invention is to decompose CFC compounds to be harmless by an atmospheric pressure plasma, without requiring an expensive plasma generation apparatus as used in prior art methods, and can easily decompose CFC compounds using a very simple apparatus, with improved effect.

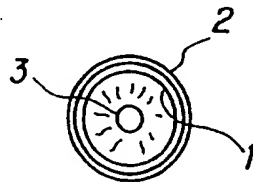
## Claims

1. A method for treating ozone layer depleting substances comprising introducing helium or argon or a mixture thereof into a plasma reactor having a dielectric-coated electrode comprising a solid dielectric disposed on the surface of at least one of opposing electrodes, generating an atmospheric pressure glow discharge in the gaseous atmosphere, introducing gaseous ozone layer depleting substances into the glow discharge to decompose the substances, and absorbing resulting decomposition products in water.

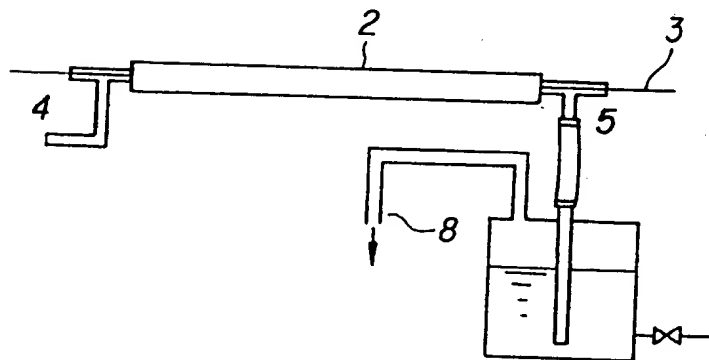
[ Fig 1 ]



[ Fig 2 ]

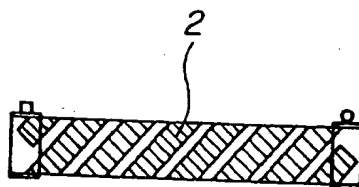


[ Fig 3 ]

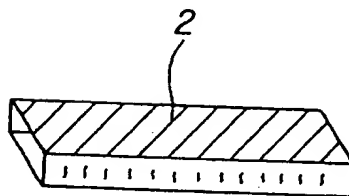




[ Fig 4 ]



[ Fig 5 ]





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# EUROPEAN SEARCH REPORT

Application Number  
EP 93 11 9722

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
X	FR-A-2 640 148 (AGENCY OF INDUSTRIAL SCIENCE AND TECHNOLOGY) * page 5, line 31 - line 34 * * page 11, line 25 - line 35 * * page 12, line 4 - line 26 *	1	A62D3/00 B01D53/34 B01D53/32
Y	---	1	
D, Y	EP-A-0 467 639 (E.C. CHEMICAL) * the whole document *	1	
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 079 (C-1027) 17 February 1993 & JP-A-42 079 179 (TOUWA KAGAKU) 5 October 1992 * abstract *	1	
X	--- CHEMICAL ABSTRACTS, vol. 118, no. 12, 1992, Columbus, Ohio, US; abstract no. 108961h, SEKIGUCHI 'Thermal plasma decomposition of chlorofluorocarbons' * abstract * & KOON GAKKAISHI vol. 18, no. 5, 1992 pages 216 - 224 -----	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 5)  A62D B01D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 March 1994	Examiner DALKAFOUKI, A
<b>CATEGORY OF CITED DOCUMENTS</b> X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document  T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons  Δ: member of the same patent family, corresponding document			